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PHASE BEHAVIOUR OF SOME MIXED CHLORIDE SALT SYSTEMS

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ABSTRACT

Phase behaviours of two different series of chloride salt mixtures, viz (a) equimolecular (NaCl + KCl), $MgCl_2$, $BaCl_2$ and (b) [NaCl + KCl], $MgCl_2$, $CaCl_2$ have been studied. The percentages of $MgCl_2$ in the salt mixtures were kept fixed at four different values viz 10, 20, 30 and 40 in these studies where other components vary. It has been found that the replacement of $CaCl_2$ with $BaCl_2$ in the four component salt mixtures does not change the shape and the temperature of the liquidus curve significantly except in the cases when the percentage of $BaCl_2$ in the mixture is more than 50.

Key Words: Phase behaviour, mixed molten salts, liquidus curve.

INTRODUCTION

The behaviour of multicomponent molten chloride salt system under different conditions is getting increased attention not only for their usefulness in the electropyrometallurgy of certain non-ferrous metals but also for their applications in the high temperature battery technology as well as in the energy storage devices [1-4]. In some earlier communications [5-7] we have reported the phase behaviour of some multicomponent chloride salt systems, particularly those related to the extraction of magnesium through molten salt electrolysis. Some comparative studies of the phase behaviour of different multicomponent chloride salt mixtures formed among the chlorides of alkaline and alkaline earth metals have also been reported recently [8]. These comparisons were done within some limited range and this paper reports the studies of phase behaviour of molten salt systems where the proportions of $MgCl_2$ were kept fixed at four different values viz. 10, 20, 30 and 40 mol per cent while the other components, (a) an equimolecular mixture of KCl and NaCl (b) $BaCl_2$ and (c) $CaCl_2$ vary.

EXPERIMENTAL

All the chloride salts used in the experiments are extrapure quality except magnesium chloride which has been supplied as anhydrous by the Nuclear Fuel Complex, Hyderabad. Such $MgCl_2$ samples were further purified by heating at about 400°C with small amount of ammonium chloride (excess of which would go due to prolonged heating) to remove any moisture contamination during storage and transport. Barium chloride was heated at about 450°C before use for removing the two molecules of water of crystallization. Care was taken during handling of the experimental salt mixtures to avoid moisture contamination from atmosphere.

Method

A muffle furnace was used for melting experiments. A Chromel-Alumel thermocouple which was frequently calibrated against melting points of standard salt mixtures and metals was used for temperature measurements. The primary crystallization points of the respective salt mixtures were noted from the corresponding cooling curves drawn with the help of a recorder (Omniscribe), and a constant current generating unit through which a known constant millivolt was applied in the opposite direction so that the difference between the experimental and the known impressed millivolt reading could be kept within 0.05 or 0.1 mV for full scale range of the recorder. This device, thus, was capable of sensing a temperature difference of 0.013°C. The overall reproducibility of the primary crystallization points was within ± 3°C.

RESULTS AND DISCUSSION

In the experimental salt mixtures, the proportions of NaCl and KCl were always kept equimolecular. With such equimolecular NaCl-KCl and $MgCl_2$, two series of four-component salt mixture systems were prepared, one by adding $BaCl_2$ and another by $CaCl_2$. The primary crystallization temperatures were determined by keeping the percentage of $MgCl_2$ in the system constant while the composition of the other components varied.

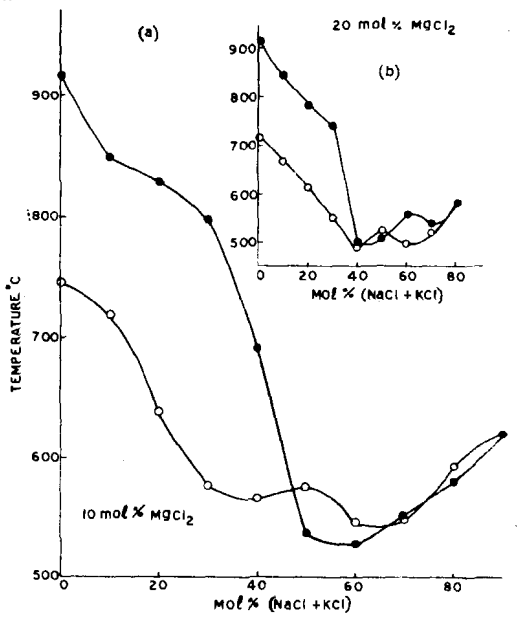

Fig. 1 (a) Comparison of the liquidus behaviours of chloride salt systems containing
○ $CaCl_2$ + (NaCl + KCl) + 10% $MgCl_2$
● $BaCl_2$ + (NaCl + KCl) + 10% $MgCl_2$

(b) Comparison of the liquidus behaviours of chloride salt systems containing
○ $CaCl_2$ + (NaCl + KCl) + 20% $MgCl_2$
● $BaCl_2$ + (NaCl + KCl) + 20% $MgCl_2$

The primary crystallization temperatures for each mixture in the above series are listed in Tables I and II. Figures 1 and 2 show the liquidus curves of the two series of the four component salt systems containing 10, 20, 30 and 40 mole percent $MgCl_2$ respectively.

Table 1: Primary crystallisation temperatures of the system $MgCl_2 — CaCl_2 — NaCl — KCl$

Composition, mol per cent				Primary crystallisation temperature °C
$MgCl_2$	$CaCl_2$	NaCl	KCl	
10	0	45	45	620
10	10	40	40	594
10	20	35	35	548
10	30	30	30	545
10	40	25	25	574
10	50	20	20	566
10	60	15	15	576
10	70	10	10	638
10	80	5	5	720
10	90	0	0	744
20	0	40	40	584
20	10	35	35	526
20	20	30	30	500
20	30	25	25	524
20	40	20	20	492
20	50	15	15	552
20	60	10	10	616
20	70	5	5	666
20	80	0	0	716
30	0	35	35	506
30	10	30	30	426
30	20	25	25	486
30	30	20	20	420
30	50	10	10	594
30	60	5	5	650
30	70	0	0	690
40	0	30	30	394
40	10	25	25	400
40	20	20	20	510
40	30	15	15	464
40	40	10	10	550
40	50	5	5	610
40	60	0	0	640

Table 2: Primary crystallisation temperatures of the system $MgCl_2 — BaCl_2 — NaCl — KCl$

Composition, mol per cent				Primary crystallisation temperature °C
$MgCl_2$	$BaCl_2$	NaCl	KCl	
10	0	45	45	620
10	10	40	40	580
10	20	35	35	550
10	30	30	30	530
10	40	25	25	536
10	50	20	20	690
10	60	15	15	800
10	70	10	10	830
10	80	5	5	850
10	90	0	0	918
20	0	40	40	584
20	10	35	35	540
20	20	30	30	560
20	30	25	25	506
20	40	20	20	500
20	50	15	15	740
20	60	10	10	784
20	70	5	5	840
20	80	0	0	916
30	0	35	35	506
30	10	30	30	490
30	20	25	25	542
30	30	20	20	468
30	40	15	15	466
30	50	10	10	784
30	60	5	5	804
30	70	0	0	896
40	0	30	30	394
40	10	25	25	475
40	20	20	20	528
40	30	15	15	452
40	40	10	10	529
40	50	5	5	734
40	60	0	0	862

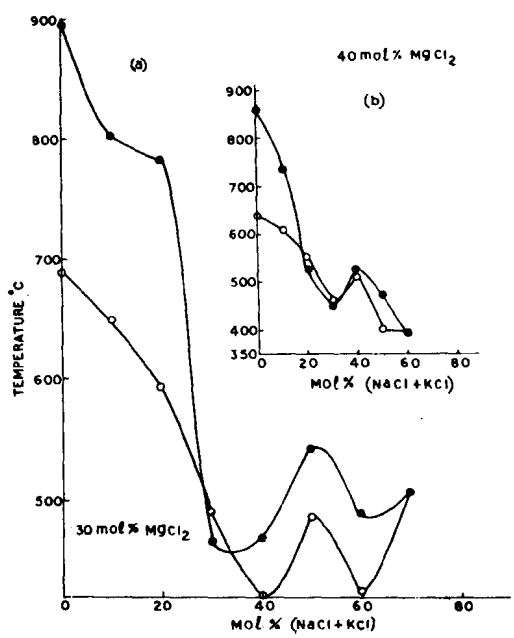

Fig. 2: (a) Comparison of the liquidus behaviours of chloride salt systems containing
○ $CaCl_2$ + (NaCl + KCl) + 30% $MgCl_2$
● $BaCl_2$ + (NaCl + KCl) + 30% $MgCl_2$

(b) Comparison of the liquidus behaviours of chloride salt systems containing
○ $CaCl_2$ + (NaCl + KCl) + 40% $MgCl_2$
● $BaCl_2$ + (NaCl + KCl) + 40% $MgCl_2$

It is evident from these figures that liquidus behaviours of the two series under study follow more or less the same trend. It is also visible that the minimum temperatures obtained in the liquidus curves of both the series as well as the composition of the mixtures corresponding to the minimum temperatures are somewhat close. It may also be noticed that the liquidus curves of the series of the $BaCl_2$ develop some tendency to stay at the higher temperature region when the percentage of $BaCl_2$ becomes as high as 60 or more. This may arise from the fact that $BaCl_2$ (mp 962°C) has a much higher melting point than $CaCl_2$ (mp 774°C). The same fact may also explain the much quicker rise in the liquidus curves of the series with $BaCl_2$ than in the curves of the series with $CaCl_2$ where the proportions of equimolecular NaCl-KCl becomes progressively less.

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